

Abiotic and Biological Degradation of Atmospheric Proteinaceous Matter Can Contribute Significantly to Dissolved Amino Acids in Wet Deposition

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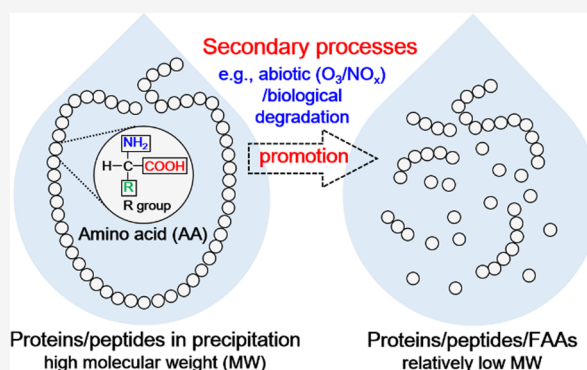


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Supporting Information

ABSTRACT: Atmospheric proteinaceous matter is characterized by ubiquity and potential bioavailability. However, little is known about the origins, secondary production processes, and biogeochemical role of proteinaceous matter in wet deposition. Precipitation samples were collected in suburban Guiyang (southwestern China) over a 1 year period to investigate their chemical components, mainly including dissolved combined amino acids (DCAAs), dissolved free AAs (DFAAs), and nonleachable particulate AAs (PAAs). Glycine was most abundant in the DFAAs, while the dominant species in DCAAs and PAAs was glutamic acid (including deaminated glutamine). The total DCAA, DFAA, and PAA concentrations peaked on average in spring (min. in summer). On average, the contribution of DCAA-nitrogen (median of 3.44%) to dissolved organic nitrogen was 5-fold higher than that of DFAA-nitrogen (median of 0.60%). Correlation analyses of AAs with ozone, nitrogen dioxide, and the quantitative degradation index suggest that DC(/F)AAs are linked with both abiotic and biological degradation of proteinaceous matter. Moreover, the high FAA scavenging ratios indicate the presence of postdepositional degradation of atmospheric proteinaceous matter. Further, the positive matrix factorization results suggest that the degradation of atmospheric proteinaceous matter markedly contributes to DCAAs and DFAAs in precipitation. Overall, the results suggest that the secondary processes involved in the degradation of atmospheric proteinaceous matter significantly promote direct bioavailability of AA-nitrogen.



INTRODUCTION

Amino acids (AAs) are ubiquitous and important organic nitrogen (ON) components in aerosols, constituting not only proteins and peptides (combined AAs, CAAs) but also free molecules (free AAs, FAAs).¹ Proteinaceous matter (FAAs and CAAs) affects the formation, chemical transformations, hygroscopicity, and acidity of organic aerosols as well as human health and regional climate.^{1–7} Subsequent wet and dry deposition eventually returns this proteinaceous matter to terrestrial and aquatic environments, which significantly contributes to the global biogeochemical cycling of nutrients.^{8,9} In recent years, an increasing number of studies have been conducted on the chemical identification of AA compounds in aerosol particles.^{4,10–15} Moreover, it is suggested that the concentrations of aerosol AAs present in free form are typically four to five times lower than those in a combined form.^{8,13,16,17} However, the proteinaceous matter in precipitation remains largely uncharacterized. This knowledge gap causes considerable unknowns in the fate and biogeochemical role of postdepositional atmospheric AAs.

To date, there are only a few available reports on AAs in precipitation. For example, Mopper and Zika¹⁸ carried out the first analyses of dissolved free AAs (DFAAs) in precipitation,

suggesting that AAs in marine precipitation could input locally available N into the sea surface. A study conducted in coastal areas (Tasmania island) found that DFAAs contributed ~53% of dissolved ON (DON) in precipitation.¹⁹ Similarly, Kieber et al.²⁰ reported a high proportion (~17%) of DFAAs in DON in precipitation in coastal areas (southeastern North Carolina). Furthermore, the authors deduced that these DFAAs can markedly affect short-term bioavailable N budgets in estuaries.²⁰ A more recent investigation on total hydrolyzed AAs in precipitation in coastal areas (Korea) also suggested that AAs constitute an important fraction of water-soluble organic matter.⁹ Notably, no study has simultaneously focused on both DFAAs and dissolved combined AAs (DCAAs) in precipitation. Additionally, water-insoluble constituents have been neglected in the same sample.^{21,22} In general, the compositions and levels of each type of AA in precipitation in

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inland areas far from the sea are poorly understood, especially for DCAAs and nonleachable particulate AAs (PAAs). A better understanding of various types of AAs in precipitation may provide useful insights into the atmospheric processes of proteinaceous matter and atmosphere–biosphere N cycling.

The levels and types of AAs in the atmosphere vary widely, which is primarily dependent on their origins and the atmospheric processes in which they are involved.¹ Owing to the low volatility of AAs, primary aerosol particles are believed to be one of the major sources of atmospheric proteinaceous matter.^{23,24} These primary aerosol particles can have either biological (e.g., pollen, bacteria, fungi, and spores) or anthropogenic (e.g., textile mill emission, biomass burning, and fertilization) origins.^{1,23,25} In addition, proteinaceous matter in aerosol particles can be decomposed to form low-molecular-weight FAAs and proteins/peptides via thermally, photochemically, and microbially mediated processes.^{14,18,26,27} More specifically, laboratory simulation experiments have observed that the oxidation of proteins/peptides by hydroxyl radical and ozone in abundant aqueous solutions can result in the release of DFAAs.^{28,29} Bacteria-induced FAA release in the atmosphere may be less important than abiotic photochemical aging of proteinaceous matter.⁹ However, these bacteria-linked processes have been reported to likely occur on aerosol particles and in cloud water.^{30,31} Indeed, due to the limited knowledge on the origins and degradation processes of proteinaceous matter in precipitation, large uncertainties exist in the relative impacts of primary and secondary (e.g., abiotic and biological degradation) production processes on DCAA and DFAA abundances in wet deposition. These secondary production processes may promote the direct bioavailability of atmospheric proteinaceous matter.

Here, we present measurements for dissolved proteinaceous matter (DCAAs and DFAAs) and PAAs in precipitation as well as some other key components in precipitation and aerosol particles from a suburban site in Guiyang city (southwestern China) during a 1 year period. This study aimed to investigate the levels and origins of dissolved proteinaceous matter and PAAs in inland precipitation without a significant impact from the sea. We also examined the factors controlling the levels of dissolved proteinaceous matter and PAAs in precipitation, with a special focus on the relative impacts of primary and secondary production processes on dissolved AA levels in precipitation.

■ EXPERIMENTAL SECTION

Site Description. Guiyang city is a typical inland city, with abundant rainwater and sunshine.³² Such a suitable environment provides favorable conditions for agricultural production and vegetation growth,³³ which are closely linked with proteinaceous matter releases. The sampling site (26.65°N, 106.62°E) is located at the Institute of Geochemistry, Chinese Academy of Sciences, which is characterized by a suburban area with little influence from urban pollution inputs. There are four atmospheric environmental monitoring stations within 4 km of the sampling site, which makes this region ideal for timely evaluation of atmospheric conditions. The air masses arriving at the sampling site in the investigated precipitation events primarily originated from the northern China and southeastern ocean areas in spring, from the southeastern and southwestern ocean areas in summer, and from local areas with a relatively short transport pathway in autumn and winter (Figure S1).

Sample Collection and Measurements. The samplings were made on a five-story building rooftop without pollution sources from May 2017 to April 2018. The rainwater sampler is composed of a large polyethylene funnel joined to a polyethylene bottle. Two sets of this equipment were cleaned and dried prior to deployment. To minimize the impacts of dry deposition on samples, the samplers were manually placed before the precipitation event and retrieved after collecting rainwater samples (<1 h of exposure to rainless weather in daytime and <5 h in nighttime). In addition to several shower events in summer, the sampling duration was strictly controlled within 24 h in most cases. Ultrapure water (Milli-Q) was added into the sampler as a blank sample. The precipitation samples were immediately filtered with precombusted 0.7 μm glass fiber filters in a nearby laboratory. The filters with intercepted particles were also collected as nonleachable particulate samples. The masses of intercepted particles were calculated by scaling the mass difference of filters before and after sample filtering. At several specific times (mainly in July to August 2017 and March 2018), total suspended particulate samplings were also performed simultaneously using a medium volume sampler for 24 h every day. All samples were kept frozen at $-30\text{ }^{\circ}\text{C}$ until analysis.

AAs were analyzed using a widely reported high-performance liquid chromatography method (HPLC 1260, Agilent Technologies, USA).^{33–35} Prior to analysis, AA extraction procedures were performed sequentially as described below. After adjusting the pH to 1 and adding internal standards (α -aminobutyric acid and sarcosine), 200–500 mL of rainwater was passed through a cation-exchange column (Dowex 50 W \times 8 H⁺, 200–400 mesh size, Sigma-Aldrich). The filtrate was collected and then passed through the cation-exchange column again. The enriched AAs were then eluted with 10 mL of 10% aqueous ammonia. Later, the eluent was filtered through a syringe filter (0.22 μm) and freeze-dried. Freeze-dried samples were eventually redissolved with 100 μL of 0.1 M hydrochloric acid solution (HCl) for DFAA analysis.

The other 40 mL (20 mL for few samples) of filtered rainwater was freeze-dried and redissolved in 2 mL of 0.1 M HCl. The redissolved samples with the addition of ascorbic acid solution and internal standards were hydrolyzed using 2 mL of HCl (12 M) in a N₂-bubbled and sealed tube at 110 $^{\circ}\text{C}$ for 24 h. Subsequently, the hydrolysate that underwent filtering (with a 0.22 μm syringe filter) and N₂ blowing (1 h) was freeze-dried. These concentrated samples were redissolved in 0.1 M HCl for the following AA analyses. The concentrations of DCAAs in the precipitation were computed by subtracting the amount of DFAAs from those detected after acid hydrolysis.

After adding the ascorbic acid solution and internal standards, the nonleachable particulate samples were directly hydrolyzed and then dried using the same method as described for rainwater samples. Eventually, the sample volumes were quantified to 100 μL using 0.1 M HCl for the determination of AAs. In addition, a portion of the filter sample ($\sim 60\text{ m}^3$ of air) was selected for the extraction of FAAs in aerosol particles. After the addition of internal standards, the sample was ultrasonically extracted twice with 5 mL of water for 25 min ($\sim 4\text{ }^{\circ}\text{C}$). The extracting solution was filtered (0.22 μm) and freeze-dried. Then, the lyophilized extracts were redissolved in 100 μL of 0.1 M HCl for aerosol FAA analyses.

The specific AA analysis method is described in the Supporting Information. Furthermore, Figure S2 shows a

typical chromatogram of the AA standard solution, which included glutamic acid (Glu), aspartic acid (Asp), asparagine (Asn), serine (Ser), glutamine (Gln), histidine (His), glycine (Gly), threonine (Thr), citrulline (Cit), arginine (Arg), alanine (Ala), γ -aminobutyric acid (GABA), theanine (Thea), tyrosine (Tyr), α -aminobutyric acid (AABA), cystine (Cy2), valine (Val), methionine (Met), norvaline (Nva), tryptophan (Trp), phenylalanine (Phe), isoleucine (Ile), ornithine (Orn), leucine (Leu), lysine (Lys), hydroxyproline (Hyp), sarcosine (Sar), and proline (Pro). Up to 21 AAs can be detected in our samples based on the above HPLC method. The correlation coefficients, precisions, recoveries (57.5–126.1%), and determination limits (0.12–6.68 pmol μL^{-1}) of AA analysis are detailed in Table S1. The concentrations of AAs in blank samples were below the determination limits.

The concentrations of total dissolved nitrogen (TDN) in the precipitation were measured using a total organic carbon/total nitrogen analyzer (Elementar, Frankfurt, Germany) with a detection limit of 0.1 mg L^{-1} .³⁴ An ICS-90 ion chromatography system (Dionex, California, USA) was applied to detect the concentrations of major water-soluble inorganic ions, such as SO_4^{2-} , NO_3^- , and Na^+ .³⁶ Nessler's reagent spectrometry with a detection limit of 0.1 mg L^{-1} was utilized to determine the concentrations of NH_4^+ in samples.³⁷ The relative standard deviations of replicate measurements of standard samples were less than 5%, 2%, and 2% for TDN, NH_4^+ , and NO_3^- , respectively. The DON concentration was defined as the difference between TDN and dissolved inorganic nitrogen (the sum of NH_4^+ , NO_3^- , and NO_2^-).³⁸

Auxiliary Data. The Global Data Assimilation System (GDAS) dataset used to calculate back trajectories was obtained from the database of NOAA's Air Resources Laboratory (<https://ready.arl.noaa.gov/archives.php>). The meteorological data (e.g., temperature, humidity, wind speed, amount of rainfall, and atmospheric pressure) and the concentrations of nitrogen dioxide (NO_2) and EPA designated 8 h ozone (O_3) during the sampling period were obtained from previously mentioned environmental monitoring stations.

Statistical Analyses. To determine the long-distance transport trajectories of the air masses arriving at the sampling site in every investigated precipitation event, MeteInfoMap (version 1.4.9R2) software (Chinese Academy of Meteorological Sciences, China) coupled with a TrajStat program (version 1.4.4R5) was applied to create 5 day (120 h) back trajectories of these air masses starting at 500 m above sea level. The quantitative degradation index (DI) for precipitation samples was computed on the basis of the molecular compositions of the AAs (Supporting Information).^{39–41} In several specific periods, the scavenging ratio (SR) for atmospheric FAAs was also calculated via the concentrations of FAAs in precipitation and aerosol particles (Supporting Information).¹⁹ A positive matrix factorization (PMF) model (version 5.0) was used to reveal the sources of the dissolved proteinaceous matter in the precipitation (Supporting Information). Regression analysis was performed via both Origin 9.0 (OriginLab Corporation, USA) and SPSS 19.0 (SPSS Science, USA) to explore potential relationships in the response and explanatory variables. Origin 9.0 software was also used to carry out principal component analysis (PCA) and plot figures. Spearman's correlations between response and explanatory variables were calculated using R software (the R Core Team, Vienna, Austria) with the corrplot package.⁴²

RESULTS AND DISCUSSION

Compositions and Concentrations of Various Types of AAs in Precipitation. Figure 1 compares the differences in

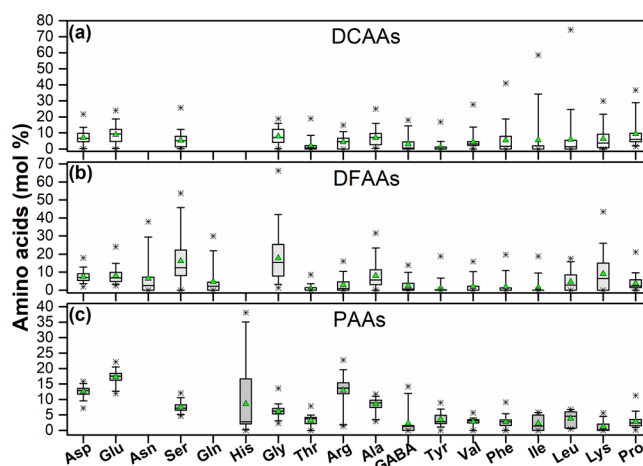


Figure 1. Molar compositions of (a) DCAAs, (b) DFAAs, and (c) PAAs in precipitation collected from suburban site in Guiyang. Each box encompasses the 25th–75th percentiles; whiskers are the 5th and 95th percentiles. The solid lines and green triangles inside boxes indicate the median and mean. The asterisks above and below the boxes denote the maximum and minimum values, respectively.

the molar compositions of total DCAAs, DFAAs, and PAAs in precipitation samples collected in an inland suburban site. Descriptive statistics for some dominant AAs are also summarized in Table S2. The concentrations of total DCAAs in precipitation varied between 291.28 and 8922.89 nM, with a volume-weighted average (VWA) of 2772.24 nM. Glu, Ala, Gly, and Pro relatively prevailed in the DCAAs. The total DFAA concentrations ranged from 136.61 to 1448.82 nM (VWA = 534.13 nM). The average concentrations of total DFAAs were approximately five times lower than those of total DCAAs, and Gly, Ala, Ser, and Lys were the relatively abundant AAs. Of particular concern is that Gly was a more dominant species in DFAAs than in DCAAs, implying that Gly could be more decomposed and reserved in the atmosphere than other AAs.

The concentrations of total PAAs measured in particles in precipitation were in the range of 22.88–209.62 mg g^{-1} , with an average of 89.88 ± 41.93 mg g^{-1} (Table S2). Glu was found to be the predominant compound followed by Arg, Asp, and Ala. This composition of PAAs was distinct from those exhibited in DCAAs and DFAAs, which likely implies varying contributing sources for PAAs.

The relative predominance of Gly among dissolved proteinaceous matter has been reported by Yan et al.⁹ for precipitation samples collected from a coastal rural area of Korea (3.4–462.0 nM) and a coastal urban site in Korea (6.4–653.0 nM). It was also well documented that Gly represented major fractions in both aerosol FAA and CAA pools.^{14,16,17,43} Gly is substantially enriched in animal fibrous proteins (collagen), elastin, and certain keratins as well as in plant tissues.^{13,35,44,45} Because Gly lacks an oxidation-sensitive side chain, the low steric hindrance for the initial radical generation on the polypeptide backbone can facilitate its release from the peptide chain, particularly when it is in the carbon-terminal region.^{29,46} Moreover, Gly has been reported to show low photochemical reactivity, with a half-life over 2000 h in the

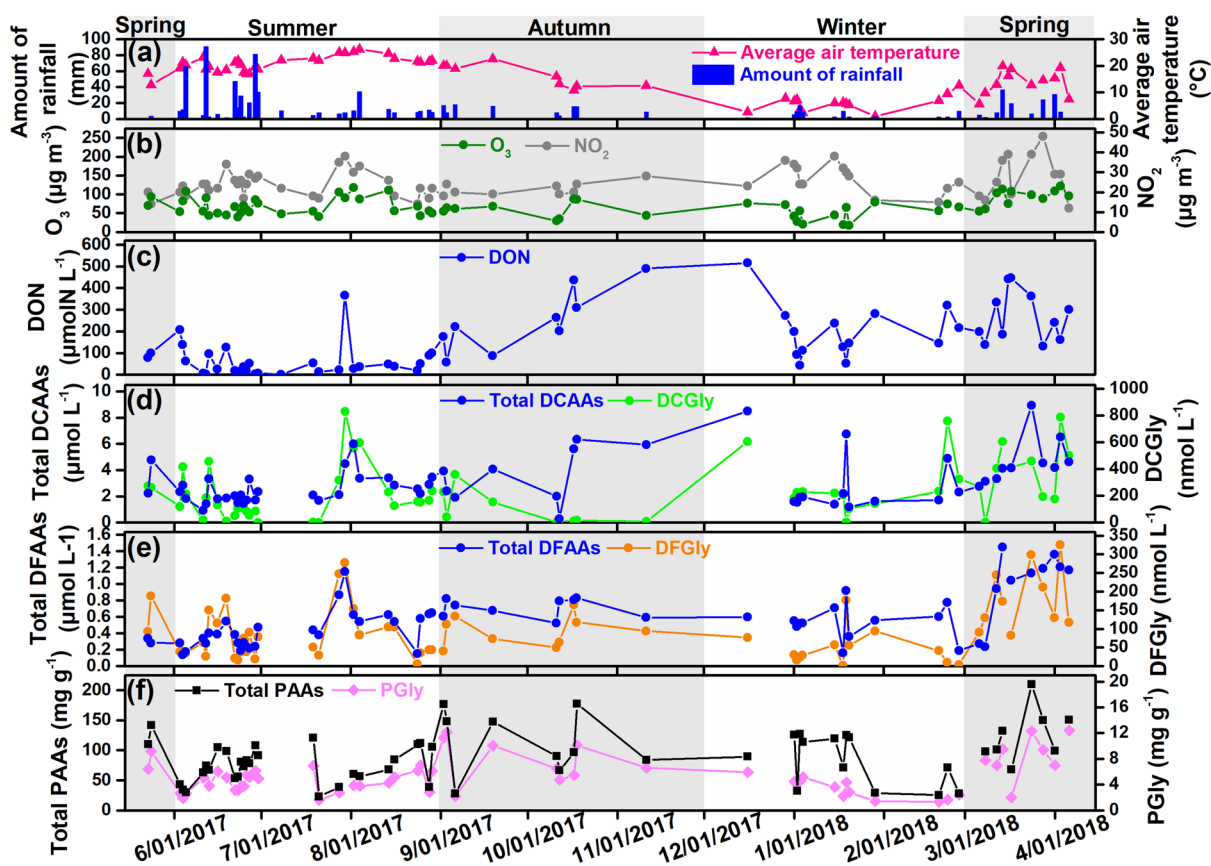


Figure 2. Temporal variations in (a) daily rainfall amounts and average air temperatures, (b) O_3 and NO_2 concentrations, (c) DON concentrations, (d) total DCAA and DCGly concentrations, (e) total DFAA and DFGly concentrations, and (f) total PAA and PGly concentrations.

aqueous phase (in contrast, the value is 23 h for Tyr and 21 h for Phe).^{14,28} Therefore, Gly is one of the most abundant AAs for dissolved proteinaceous matter in precipitation.

The levels of other important dissolved AAs, including Glu, Ser, Ala, Pro, Asp, and Lys, in precipitation were generally comparable to those measured in some aquatic environments as well as snow, ice, and aerosol particle samples.^{4,8,27,47,48} This observation is attributable to the fact that those AAs are also extensively distributed in the plant and animal kingdoms.^{4,33,49–51} As reported by previous studies, continental primary biological aerosol particles related to plant and animal debris can serve as a major source of atmospheric proteinaceous matter.^{1,4,23,24}

PAAs in precipitation are expected to be closely associated with aerosol particles and cloud condensation nuclei as a result of rainout and washout effects. However, a limited number of existing studies have reported measurements of PAAs in precipitation, making it difficult to perform a direct comparison with different data sets. Interestingly, a high Arg abundance in PAAs was consistent with the observations by Mace et al.⁵² for Arg levels in aerosol particles. In their study,⁵² Arg showed a significant dominance in PM_{10} collected from the forested Amazon during both the wet and dry seasons. Moreover, the authors attributed this result to the impacts of primary biological aerosol particles and biomass burning. Pollen collected in Ankara, Turkey, has been found to be rich in Arg.⁵³ Abundant Arg observed in forest aerosol particles in Hyytiälä, Finland, was also attributed to the contribution of pollen.⁴ In particular, previous studies conducted in the same

area as this study have suggested that Arg is one of most abundant AAs in moss, Masson pine, and camphor tissues.^{33,35} Therefore, in this study area, with widespread forest and frequent agricultural activities, relatively high total PAA and PArg levels in precipitation may also be linked with primary biological sources, which will be investigated further in the following discussion.

Temporal Variations of The Concentrations of Various Types of AAs in Precipitation. Figure 2 presents the time series for the rainfall amounts, air temperatures, and gaseous pollutant levels as well as the concentrations of DON and different types of AAs in precipitation. We observed four distinct seasons, with a rainy and mild summer and spring together with a relatively rainless and cold autumn and winter. Following the varying climate, DON in precipitation displays a clear seasonal cycle with higher mean levels in spring and autumn than in summer and winter. The temporal variation of the total DCAA concentrations was comparable to that of the DON concentrations ($r = 0.55$, $P < 0.001$), likely indicating similar sources for them. On average, the total DCAA-N represented 7.6% of DON-N (median = 3.44%). The temporal trend of DCGly, which is an abundant component in DCAAs, also followed that of DON in spring, summer, and late winter. In autumn, DCGly showed a distinctly inconsistent variation pattern in concentrations with DON and total DCAAs, which suggested a varying source or formation process for DCGly.

The concentrations of total DFAAs showed similar temporal trends with that of total DCAAs across the sampling period excluding late autumn and early winter (Figure 2d,e).

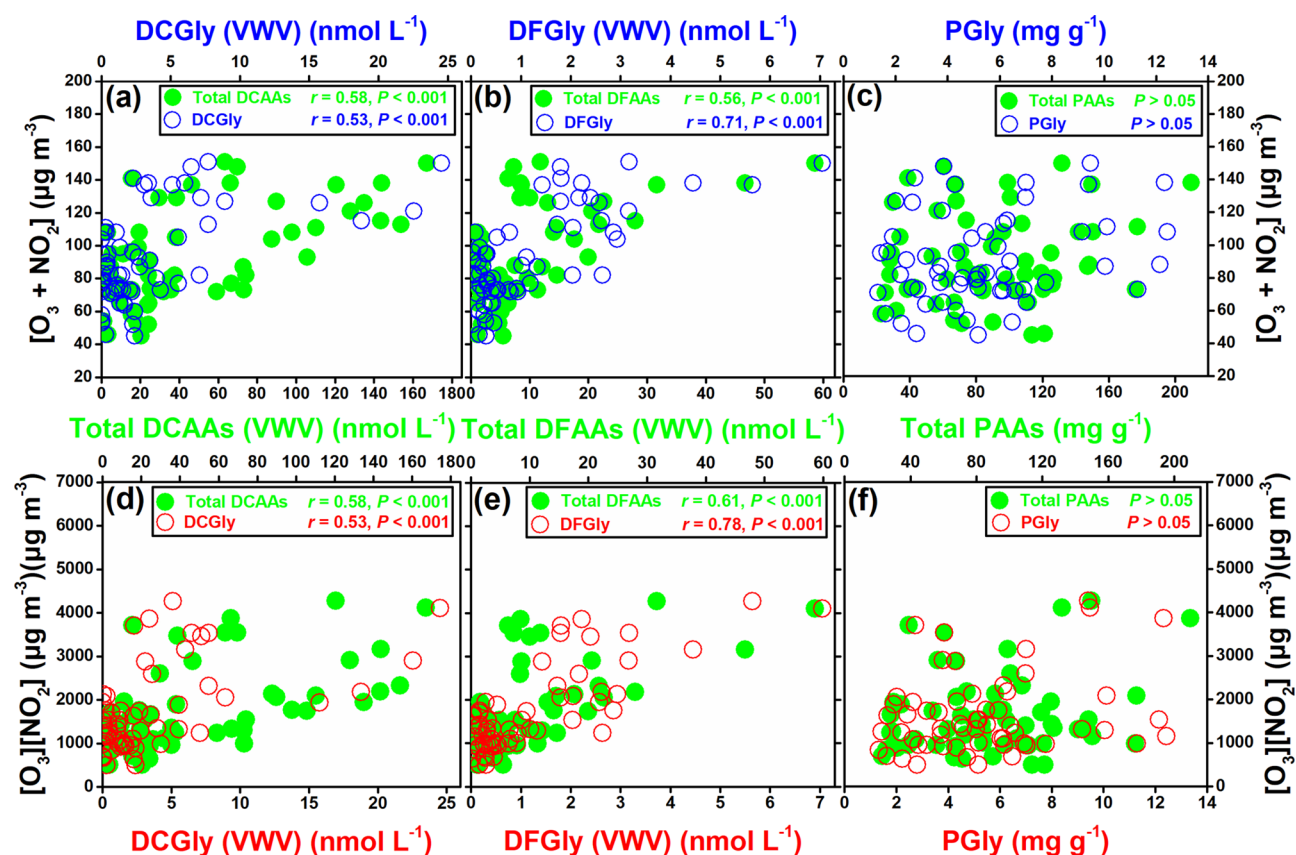


Figure 3. Linear relationships of the concentrations of different types of amino acids in precipitation with ambient O_3 and NO_2 concentrations: (a) total DCAAs and DCGly vs $[NO_2 + O_3]$, (b) total DFAAs and DFGly vs $[NO_2 + O_3]$, (c) total PAAs and PGly vs $[NO_2 + O_3]$, (d) total DCAAs and DCGly vs $[NO_2][O_3]$, (e) total DFAAs and DFGly vs $[NO_2][O_3]$, and (f) total PAAs and PGly vs $[NO_2][O_3]$. The volume-weighted value (VWV) was calculated via the individual rainfall amount in every investigated precipitation event and the total rainfall amount throughout the whole investigation period.

Moreover, total DFAA-N contributed 1.45% of DON-N on average (median = 0.60%). In particular, the time series of total DFAAs maintained a relatively strong consistency with DFGly ($r = 0.65$, $P < 0.001$). The similarity in temporal trends of total DCAAs, total DFAAs, and DFGly implied that their sources or formation processes are similar.

Since rainfall amounts could lead to a marked impact on species abundance in precipitation, we also compared the seasonal differences in the VWAs of the investigated species. On average, the VWAs of total DCAA, DCGly, total DFAA and DFGly were higher in spring and summer than in autumn and winter (over 33% seasonal differences), which resembled the seasonal variation of O_3 levels (over 27% seasonal differences) (Figure 2b). These results suggested that the dissolved AAs in precipitation may also be linked with O_3 -induced atmospheric processes.

The total PAA concentrations also exhibited a clear seasonal cycle with relatively high average levels in spring and autumn (Figure 2f), a pattern which has been observed in total DCAA and DFAA concentrations. More specifically, with the exception of midsummer, late autumn, and early winter, the time series of total PAA concentrations present a strong resemblance to those of total DCAA and DFAA concentrations. Moreover, the total PAA concentrations were significantly correlated with the PGly concentrations ($r = 0.85$, $P < 0.001$). These results suggested similar speciation or interconnected atmospheric processes in dissolved and particulate proteinaceous matter.

Although there are currently no published data about PAAs in precipitation, the seasonal patterns of FAAs/CAAs in aerosol particles have been widely investigated by many previous studies.^{3,11,12,14,54} It was found that the concentrations of aerosol FAAs and CAAs were commonly higher in spring or summer than in winter for these investigations in Roma,³ North Carolina,⁵⁵ and Iowa.¹¹ The expectation that PAA concentrations should be higher in spring or summer than in winter is also confirmed in this work. However, enhancements of proteinaceous matter (e.g., FAAs and proteins) in aerosol particles occurred in late autumn and winter in Hefei (eastern China),²⁵ Guangzhou (southern China),¹⁴ and Hong Kong (coastal China).⁵⁴ Different sources and atmospheric processes in different areas can be responsible for the seasonally different variations in proteinaceous matter in atmospheric particles.¹⁴

The Degradation of Atmospheric Proteinaceous Matter. Figure 3 shows the concentrations of different types of AAs in precipitation as functions of the sum ($[O_3 + NO_2]$) and products ($[O_3][NO_2]$) of the O_3 and NO_2 concentrations. Although the total DCAA, DCGly, total DFAA, and DFGly concentrations were also significantly correlated with the ambient O_3 levels ($r = 0.50$ – 0.63 , $P < 0.05$), the correlations of those dissolved proteinaceous matter concentrations with $[O_3 + NO_2]$ and $[O_3][NO_2]$ were stronger than those with only O_3 , particularly for total DFAAs and DFGly (Figure 3). Presumably, mixed O_3 - and NO_2 -related atmospheric processes are more conducive to the release of relatively low-

molecular-weight AAs.²⁷ However, we did not observe an expected negative correlation in atmospheric reactive species and both PGly and total PAA concentrations (Figure 3c,f), likely implying that abiotic degradation of particulate proteinaceous matter has a limited impact on PAA abundance. In addition, both average and daily maximum temperatures showed significant positive correlations with the total DCAA, DCGly, total DFAA, and DFGly concentrations (Table S3), suggesting that temperature can serve as an important factor controlling the degradation of proteinaceous matter in precipitation (e.g., thermal decomposition).¹⁹

Previous studies have reported that O₃ is able to cause the release of proteinaceous matter from pollen, resulting in an enhanced biological aerosol level.^{56,57} Recent field investigations on aerosol FAAs have also confirmed the O₃-induced release of low-molecular-weight AAs from proteins and peptides.¹⁴ Considering the fast production of hydroxyl radical ($\cdot\text{OH}$) in the processes of O₃ photolysis,⁵⁸ $\cdot\text{OH}$ should also play an important role in O₃-induced proteinaceous matter degradation. As expected, a recent laboratory study provided direct evidence for the involvement of $\cdot\text{OH}$ in proteinaceous matter degradation.²⁹ Moreover, laboratory simulation experiment involved in protein ozonation suggested that water can significantly promote O₃-induced protein oxidation and degradation,^{59,60} which partly supports the strong correlation of dissolved AA and O₃ concentrations ($P < 0.05$). A plausible explanation is that O₃ can diffuse and react faster in humid proteinaceous matter than in dry proteinaceous matter.⁵⁹

In addition, a simulated experiment by Shiraiwa et al.⁶⁰ has suggested that proteins on the surface of aerosol particles can be rapidly nitrated with continuous exposure to NO₂. Similar nitration of proteins by NO₂ was also found in the polluted urban atmosphere.⁶¹ In fact, the reactivity of NO₂ is weaker than those of general atmospheric oxidants (e.g., $\cdot\text{OH}$, O₃, and nitrate radical). Thus, the high-molecular-weight proteinaceous matter first reacts with O₃/ $\cdot\text{OH}$ /nitrate radical to generate reactive intermediates, which then react with NO₂ to form new compounds or cause the release of FAAs.^{27,62,63} Further, it is conceivable that the synergistic effect of O₃ and NO₂ (e.g., oxidation, oligomerization, and nitration^{28,61,64}) can more easily trigger the release of low-molecular-weight proteinaceous matter than their separate roles. This synergistic effect was directly reflected by stronger correlations between dissolved AAs and both [O₃][NO₂] and [O₃ + NO₂], which is also consistent with the situation that occurred on the surface of aerosol particles.²⁷

The above discussion suggested that O₃/ $\cdot\text{OH}$ -induced degradation of proteinaceous matter results in the production of DC(/F)AAs, particularly DFGly. Concurrently, these products would be further oxidized by O₃ and/or $\cdot\text{OH}$, as shown in Figure S3. However, compound-specific structures partly determine their lifetime in the atmosphere. In contrast with known reactive AAs (Figure S3), FGly without an oxidation-sensitive side chain is undoubtedly an important tracer indicating the degradation of high-molecular-weight proteinaceous matter and long-lived aerosols.^{14,15,28,29,65,66} Such a consideration also explains a more pronounced correlation in DFGly and atmospheric oxidants (Figure 3).

To assess the influence of biologically relevant degradation of proteinaceous matter on the dissolved AA levels in precipitation, the DI values were compared with the total DFAA-N and DFAA-C, total dissolved AA-N and AA-C, and their ratios, as presented in Figure 4. The DI was developed on

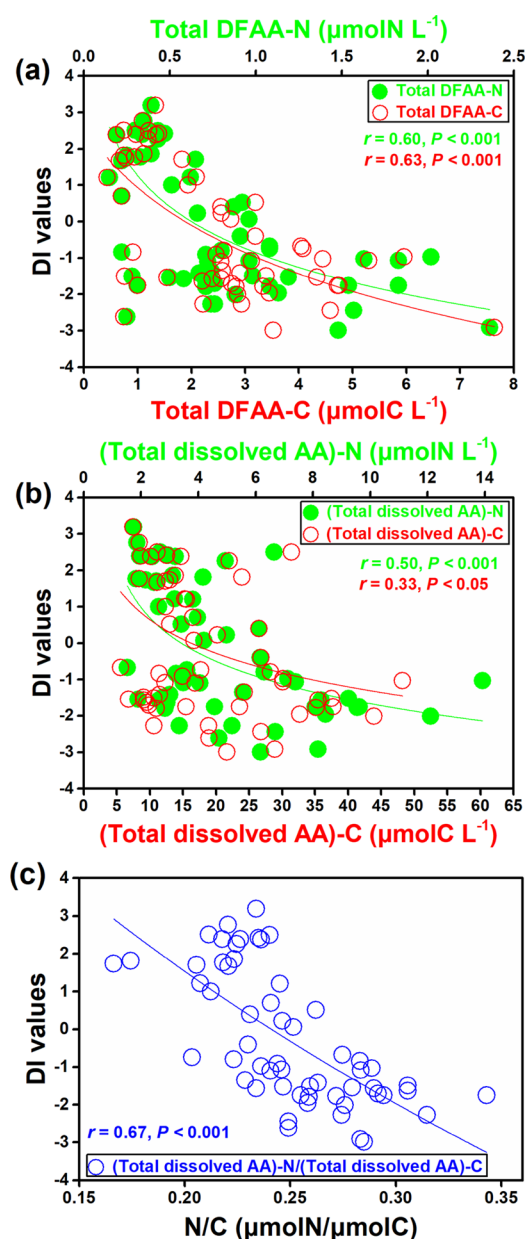


Figure 4. Logarithmic relationships of the quantitative degradation index (DI) with (a) total DFAA-N and total DFAA-C, (b) (total dissolved AA)-N (namely, total DCAA-N + total DFAA-N) and (total dissolved AA)-C (namely, total DCAA-C + total DFAA-C), and (c) (total dissolved AA)-N/(total dissolved AA)-C.

the basis of compositional variations of AA pools (Supporting Information), for which relatively low values denote relatively “old” organic matter.^{9,41,67} As shown in Figure 4a, both total DFAA-N and DFAA-C tended to logarithmically increase with an enhanced “aging process” of organic matter (lower DI values). Similarly, a logarithmic increase with decreasing DI values was observed in total dissolved AA-N and AA-C (Figure 4b). In addition, the ratio of total dissolved AA-N/total dissolved AA-C showed a significant logarithmic increase with decreasing DI values (Figure 4c), implying that the increasing rate of dissolved AA-N was higher than that of dissolved AA-C with enhancing biodegradation processes. Such nonlinear variations in the response and explanatory variables are attributable to a decrease in the degradation rates of dissolved organic matter caused by microorganisms.⁶⁸ Thus, these results

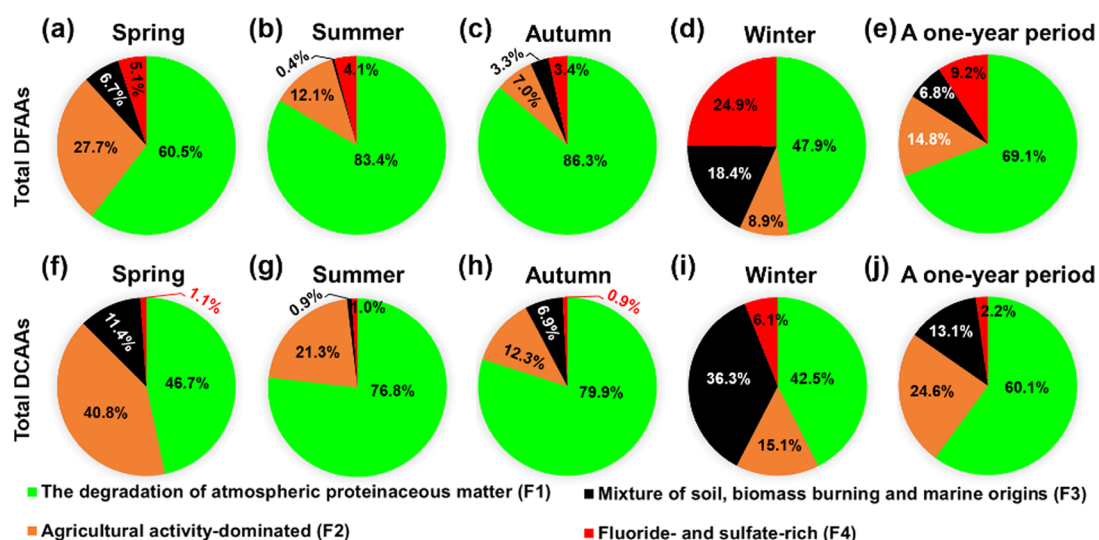


Figure 5. Illustrations of the percentage of factor contributions to the total DFAAs in (a) spring, (b) summer, (c) autumn (d) winter, and (e) a 1 year period and the total DCAAs in (f) spring, (g) summer, (h) autumn (i) winter, and (j) a 1 year period.

indicated that the dissolved proteinaceous matter in precipitation is closely related to the biodegradation of organic matter.

Tremblay and Benner⁶⁹ have reported that the N/C ratios of terrestrial organic matter (e.g., plants) generally tend to increase during the biodegradation process. This increase is because of the incorporation of N-enriched bacterial detrital biomass into residual organic matter.⁶⁹ Such enhancement of N/C ratios was also observed in the biodegradation of proteinaceous matter in precipitation, as mentioned above. An available study on DI values (based on the compositions of total dissolved AAs) for precipitation samples in the Korean Peninsula suggested that the DI values showed nonsignificantly correlations with both total dissolved AA-N and AA-C.⁹ This result implied that bacterial degradation likely played a minor role in shaping the dissolved AA pools in precipitation in coastal areas.⁹ In contrast, our study confirmed microorganism-induced degradation of organic matter to release dissolved AAs in precipitation in inland areas.

The existence of microorganisms in aerosol particles and cloud droplets has been previously documented.^{70,71} However, when these microbes are incorporated into precipitation, the biotransformation and biosynthesis of proteins/AAs will also occur simultaneously with their biological degradation. Indeed, the biological factors controlling dissolved AA levels are not well understood. In-depth research on the biochemical processes in which atmospheric proteinaceous matter is involved is necessary in the future.

Postdepositional Degradation of Proteinaceous Matter in Precipitation. To explore the postdepositional variations of dissolved AAs in precipitation, SR values for atmospheric FAAs in several specific periods were calculated (Supporting Information). In this study, the calculated average SR value was $0.9 \times 10^4 \pm 0.4 \times 10^4$, ranging from 0.5×10^4 to 1.6×10^4 (Table S4). The SR values for the aerosol phase typically varied between 200 and 2000.⁷² Because AAs are characterized by large Henry's law constants (2.0×10^5 to 1.0×10^{11} mol m⁻³ Pa⁻¹),^{73,74} gas-phase AAs contribute a negligible fraction to the dissolved AAs in precipitation.¹⁹ Therefore, the increased DFAAs in precipitation likely

suggested a postdepositional degradation of proteinaceous matter.

It is well known that precipitation contains a large number of active bacteria and fungi derived from aerosol particles and cloud droplets.^{26,70,71} These live species have been found to have the ability to metabolize organic nitrogen compounds.¹⁹ In addition, O₃-/·OH-related protein oxidation occurs concurrently in precipitation. Due to the duration required to collect sufficient precipitation samples for chemical analysis, it is possible that proteinaceous matter within precipitation underwent not only thermal and photochemical processes but also microbial enzymatic cleavage, biotransformation, and biosynthesis. The analysis of SR values for aerosol FAAs by Mace et al.¹⁹ also demonstrated a similar degradation process of organic nitrogen in precipitation.

Regarding in situ photochemical and bacterial decomposition processes of proteinaceous matter in aerosol particles and cloud droplets (known as predeposition), their occurrences have been confirmed in previous studies.^{14,27,30,31} Subsequently, proteinaceous matter in aerosol particles and cloud droplets would be incorporated into precipitation because of rainout and washout effects. Furthermore, the correlations of proteinaceous matter in precipitation with ambient oxidants and DI reflected the net effect of a range of biochemical degradation processes. Thus, the overall results indicated that the pre- and postdepositional atmospheric proteinaceous matter is involved in both abiotic and biological degradation processes. Further, these processes would eventually cause an increase in the amount of dissolved AAs in precipitation.

Major Origins of Dissolved Proteinaceous Matter in Precipitation. To reveal the potential sources of proteinaceous matter in precipitation in suburban Guiyang, correlation analysis among proteinaceous matter and other chemical components in precipitation was investigated (Figure S4). As expected from the previous discussion on AA temporal trends, significant positive correlations were observed among the concentrations of total PAAs, dissolved proteinaceous matter, DCAAs, and DFAAs. The results suggested that PAAs and dissolved proteinaceous matter have similar sources or are involved in similar atmospheric processes.

Total PAAs, dissolved proteinaceous matter, DCAAs, and DFAAs were also found to be significantly positively correlated with FGly (Figure S4). It was recently reported that FAAs, particularly FGly, in aerosol fine particles were mainly secondarily produced via photochemical decomposition of high-molecular-weight proteinaceous matter.¹⁴ As previously discussed in this study, we also confirmed that the dissolved proteinaceous matter including low reactive FGly in precipitation can be produced via both abiotic and biological degradation of proteinaceous matter. Accordingly, those dissolved and particulate AAs in precipitation were involved in similar atmospheric processes.

Both total DCAAs and DFAAs displayed significant positive correlations with NH_4^+ and NO_3^- (Figure S4). Previous studies have reported that NH_4^+ in precipitation in suburban Guiyang mainly originated from agricultural activities such as livestock wastes and fertilizers.^{32,34,75} NO_3^- in local precipitation is also primarily controlled by non-fossil-related sources including the microbial nitrogen cycle and agricultural activities.^{34,75} Therefore, agriculture-related sources could be important contributors to dissolved proteinaceous matter in local precipitation.

In addition, the total DCAA concentrations significantly correlated with crustal materials (e.g., nss-Ca^{2+} and Mg^{2+}),⁷⁶ nss-K^+ (biomass burning tracer),^{77–79} and anthropogenic nss-SO_4^{2-} and F^- sources,^{79,80} suggesting that mixed sources controlled the DCAA abundance in local precipitation. However, the total DFAA and FGly concentrations showed nonsignificant correlations with nss-Ca^{2+} , Mg^{2+} , nss-K^+ , F^- , and nss-SO_4^{2-} . This finding supported the idea that atmospheric FAAs can be derived largely from secondary production processes. In contrast, total PAAs only correlated well with nss-K^+ , implying that biomass burning would be a possible source of PAAs.

A PMF analysis was conducted to further apportion sources of the measured total DCAAs and DFAAs in precipitation. The PMF resolved four interpretable factors, as shown in Figure S5. Figure 5 presents the seasonal contributions of each factor to the total DFAAs and DCAAs in precipitation. The mass of dissolved proteinaceous matter can be primarily attributed to the degradation of proteinaceous matter (F1) during all seasons (42.5–86.3%), particularly in relatively warm seasons such as summer and autumn (76.8–86.3%). A plausible explanation is that a low temperature (i.e., in winter) is not conducive to the thermal, photochemical, and microbial degradation of proteinaceous matter. Previous studies have also documented that low temperatures can result in a decline in oxidation ability of O_3 and microbial activity.^{81–83} Moreover, F1 contributed a higher proportion to total DFAAs than to total DCAAs (Figure 5), further indicating that atmospheric FAAs were mainly derived from the degradation of high-molecular-weight proteinaceous matter.

There are relatively high agricultural contributions for both total DFAA (27.7%) and DCAA (40.8%) masses in spring (Figure 5a,f) as a result of enhancing agricultural activities in spring. In addition, other anthropogenic and natural contributions (F3 and F4) showed a significant impact on total DFAA (43.3%) and DCAA (42.4%) concentrations in winter (Figure 5d,i). This finding may be attributable to the high energy consumption for heating and local/regional air mass transport in winter (Figure S1).

Of particular note is that PMF analysis may slightly overestimate the contribution of secondarily produced

processes to total DFAA and DCAA masses as a result of the presence of a small amount of primary FGly sources. In the present study, the determination coefficient of DFAAs (e.g., Gly) with oxidants and DI showed that 61 and 36% of the variability in the FGly mass concentrations can be explained by abiotic and biological degradation processes of proteinaceous matter, respectively. In addition, Song et al.¹⁴ reported that only O_3 -induced protein degradation can explain 81% of the variability in FGly in $\text{PM}_{2.5}$ ($R^2 = 0.81$, $P < 0.01$). Thus, although it is difficult to accurately quantify FGly production by secondary processes only from correlation analysis (e.g., Figure 3 and Figure S4), the limited primary sources, at least for FGly, can be expected in this case.

The overall results suggested that the dissolved proteinaceous matter in precipitation could be substantially generated from both abiotic and biological degradation of the pre- and postdepositional atmospheric proteinaceous matter. Such degradation processes of proteinaceous matter may directly enhance the bioavailability of atmospheric organic nitrogen in surface ecosystems after deposition. Thus, this study can not only improve current knowledge of the formation and transformations of proteinaceous matter in wet deposition but also contribute important information to the biogeochemical cycle of AA-nitrogen.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.0c00421>.

Details of the AA determination, DI and SR calculations, PMF analysis, four tables (Tables S1–S4), and four extensive figures (Figures S1–S5) (PDF)

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Notes

The authors declare no competing financial interest.

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